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Published in:
European Journal of Organic Chemistry

DOI:
[10.1002/ejoc.200900084](https://doi.org/10.1002/ejoc.200900084)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

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Citation for published version (APA):

Rioz-Martinez, A., de Gonzalo, G., Pazmino, D. E. T., Fraaije, M. W., & Gotor, V. (2009). Enzymatic Baeyer-Villiger Oxidation of Benzo-Fused Ketones: Formation of Regiocomplementary Lactones. *European Journal of Organic Chemistry*, (15), 2526-2532. <https://doi.org/10.1002/ejoc.200900084>

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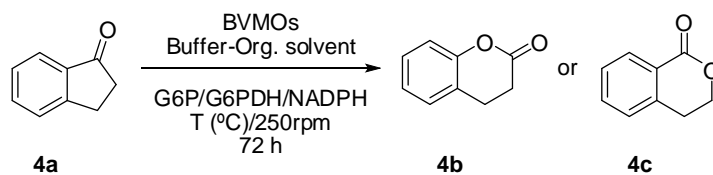
SUPPORTING INFORMATION

Title: Enzymatic Baeyer–Villiger Oxidation of Benzo-Fused Ketones: Formation of Regiocomplementary Lactones

Author(s): Ana Ríoz-Martínez, Gonzalo de Gonzalo, Daniel E. Torres Pazmiño, Marco W. Fraaije, Vicente Gotor*

Ref. No.: O200900084

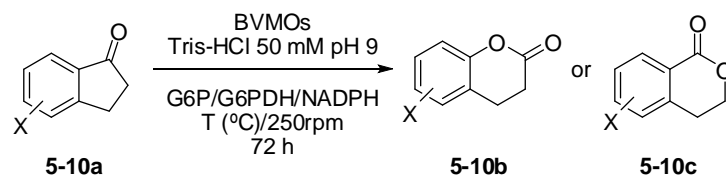
1. HAPMO and M-PAMO catalyzed oxidation of 1-indanone 4a in different buffer-organic cosolvent (5% v v⁻¹) media



Entry	BVMO	Cosolvent	log P	T (°C)	[%] 4b ^[a]	[%] 4c ^[a]
1	HAPMO	None	--	20	25	≤3
2	HAPMO	MeOH	-0.76	20	11	≤3
3	HAPMO	1,4-dioxane	-0.27	20	≤3	≤3
4	HAPMO	<i>i</i> -PrOH	0.07	20	16	≤3
5	HAPMO	CH ₂ Cl ₂	1.25	20	21	≤3
6	HAPMO	<i>t</i> BuOMe	1.35	20	25	≤3
7	HAPMO	<i>i</i> Pr ₂ O	2.00	20	35	≤3
8	HAPMO	toluene	2.50	20	34	≤3
9	HAPMO	2-octanol	2.72	20	39	≤3
10	HAPMO	hexane	3.50	20	44	≤3
11	M-PAMO	None	--	30	≤3	67
12	M-PAMO	MeOH	-0.76	30	≤3	79
13	M-PAMO	1,4-dioxane	-0.27	30	≤3	71
14	M-PAMO	<i>i</i> -PrOH	0.07	30	≤3	75
15	M-PAMO	CH ₂ Cl ₂	1.25	30	≤3	12
16	M-PAMO	<i>t</i> BuOMe	1.35	30	≤3	77
17	M-PAMO	<i>i</i> Pr ₂ O	2.00	30	≤3	82
18	M-PAMO	toluene	2.50	30	≤3	22
19	M-PAMO	2-octanol	2.72	30	≤3	47
20	M-PAMO	hexane	3.50	30	≤3	31

^[a] Determined by GC.

2. Results obtained in the BVMO-oxidation of 1-indanone derivatives 5-10a using only buffer Tris-HCl 50 mM pH 9.



Entry	Ketone	X	BVMO	T (°C)	[%] 5-10b ^[a]	[%] 5-10c ^[a]
1	5a	5-Cl	HAPMO	20	39	≤3
2	5a	5-Cl	PAMO	30	≤3	≤3
3	5a	5-Cl	M-PAMO	30	≤3	54
4	6a	6-Cl	HAPMO	20	52	≤3
5	6a	6-Cl	PAMO	30	≤3	4
6	6a	6-Cl	M-PAMO	30	≤3	52
7	7a	5-Br	HAPMO	20	6	≤3
8	7a	5-Br	PAMO	30	≤3	5
9	7a	5-Br	M-PAMO	30	≤3	57
10	8a	4-OMe	HAPMO	20	≤3	≤3
11	8a	4-OMe	PAMO	30	≤3	≤3
12	8a	4-OMe	M-PAMO	30	≤3	35
13	9a	5-OMe	HAPMO	20	13	≤3
14	9a	5-OMe	PAMO	30	≤3	≤3
15	9a	5-OMe	M-PAMO	30	≤3	26
16	10a	6-OMe	HAPMO	20	32	≤3
17	10a	6-OMe	PAMO	30	≤3	≤3
18	10a	6-OMe	M-PAMO	30	≤3	≤3

^[a] Determined by GC.

3. GC analyses

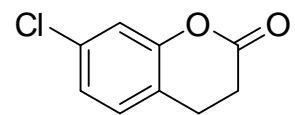
The following columns were used for the determination of conversions: A: Restek RT-BetaDEXse (30 m x 0.25 mm x 0.25 μ m, 12 psi N₂) and B: Hewlett Packard HP-1 (30m x 0.32 mm x 0.25 μ m, 12.2 psi N₂).

Table 1. Determination of conversion values by GC.

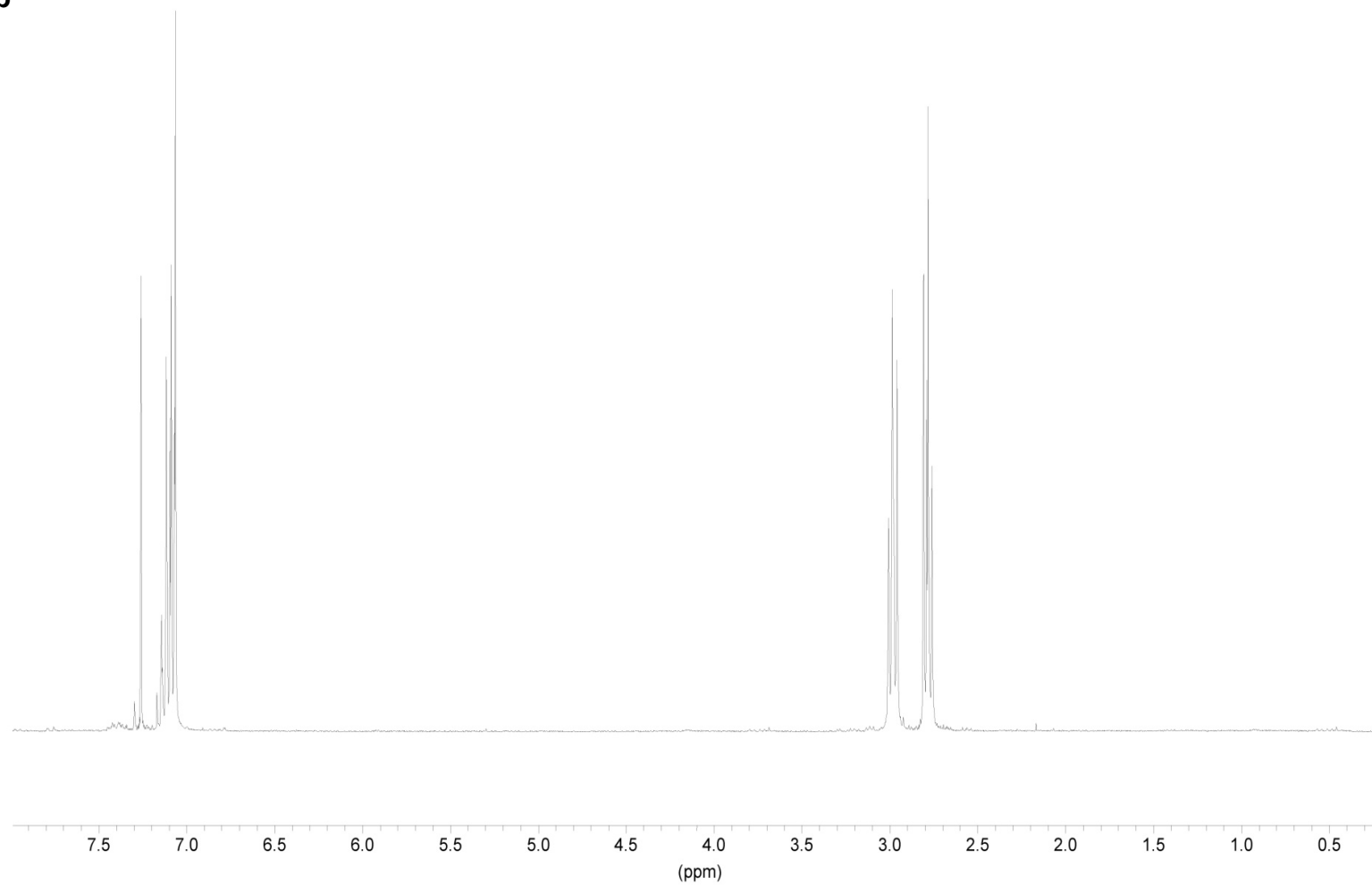
Substrate	Program ^[a]	Column	t _R [min]	t _R [min]	t _R [min]
			1-11a	1-11b	4-10c
1	70/5/3/180	A	37.1	42.2	--
3	70/5/3/180	A	32.0	45.5	--
4	70/5/3/180	A	33.5	40.1	44.1
5	70/5/3/200/5	A	41.9	48.8	51.8
6	70/5/3/200/5	A	41.5	48.0	51.9
7	100/5/2/160	B	12.7	17.4	23.9
8	100/5/3/200/5	A	34.4	39.3	44.5
9	100/5/3/200/15	A	36.1	41.0	50.1
10	100/5/3/200/10	A	33.5	39.8	42.8
11	70/5/3/180	A	22.3	29.6	--

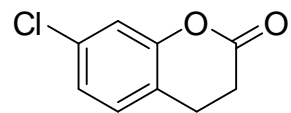
^[a] Program: initial T (°C)/ time (min)/ slope (°C/min)/T (°C)/ time (min)/

4. NMR Spectra

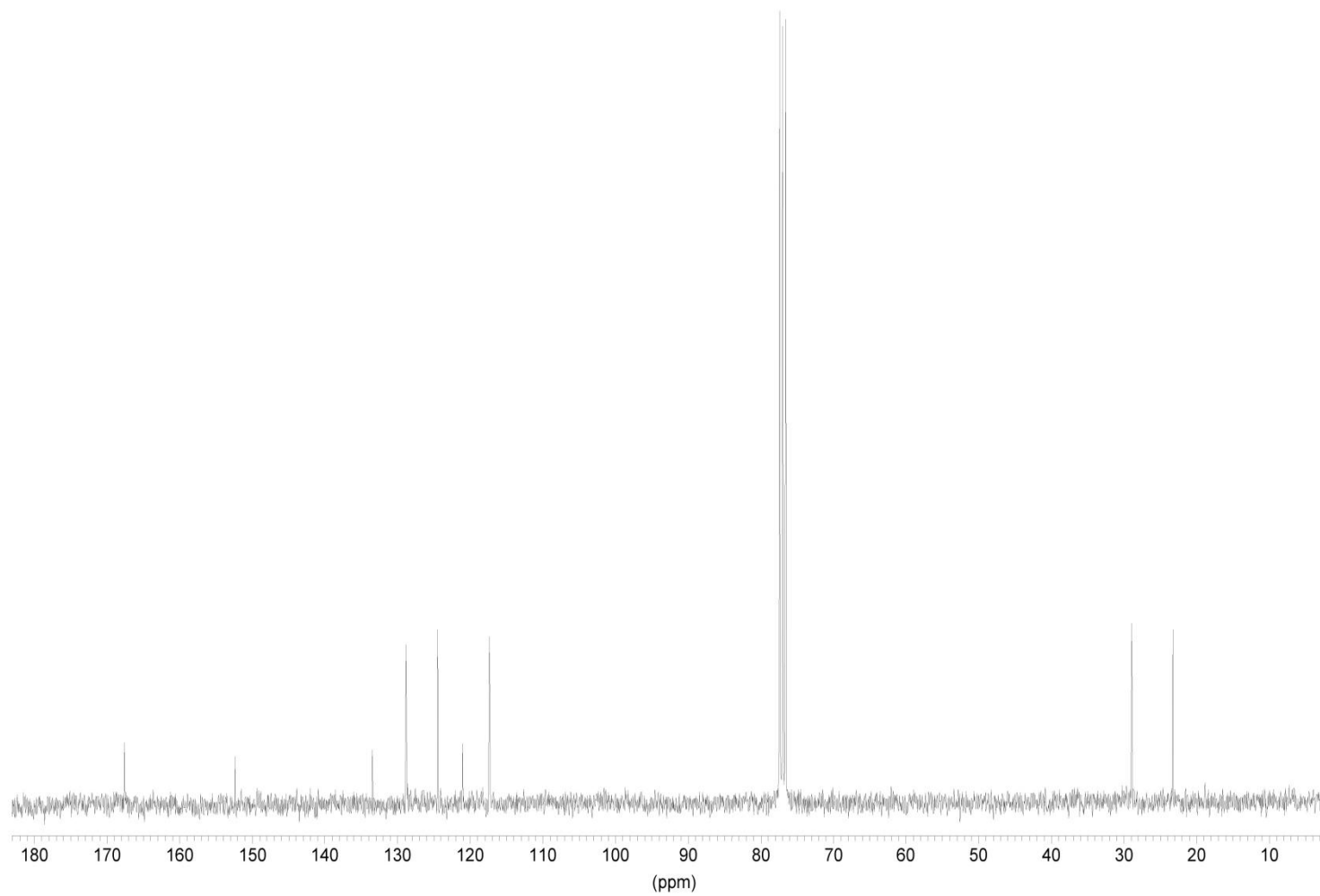


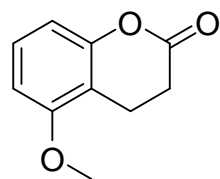
(±)-**6b**



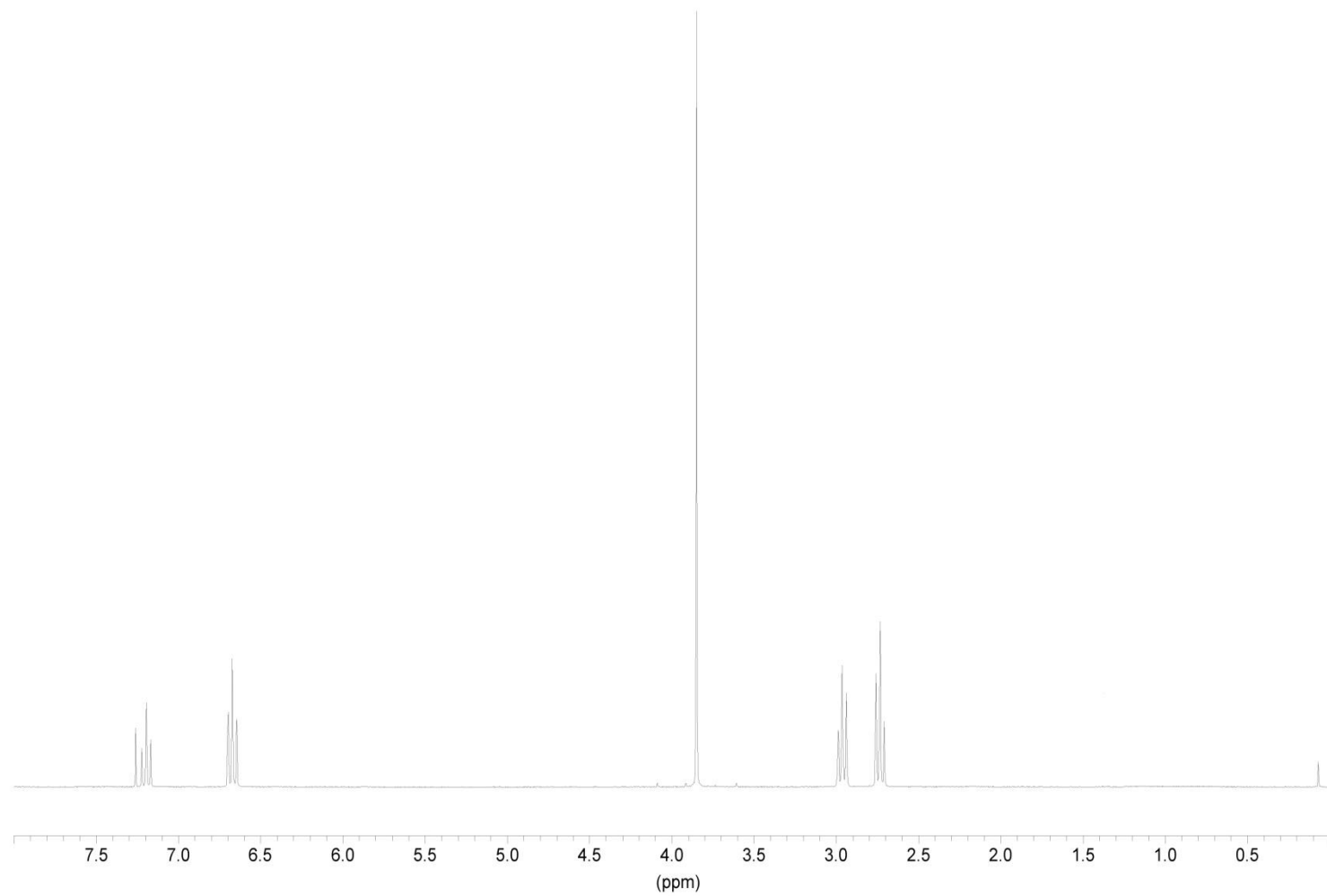


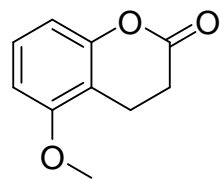
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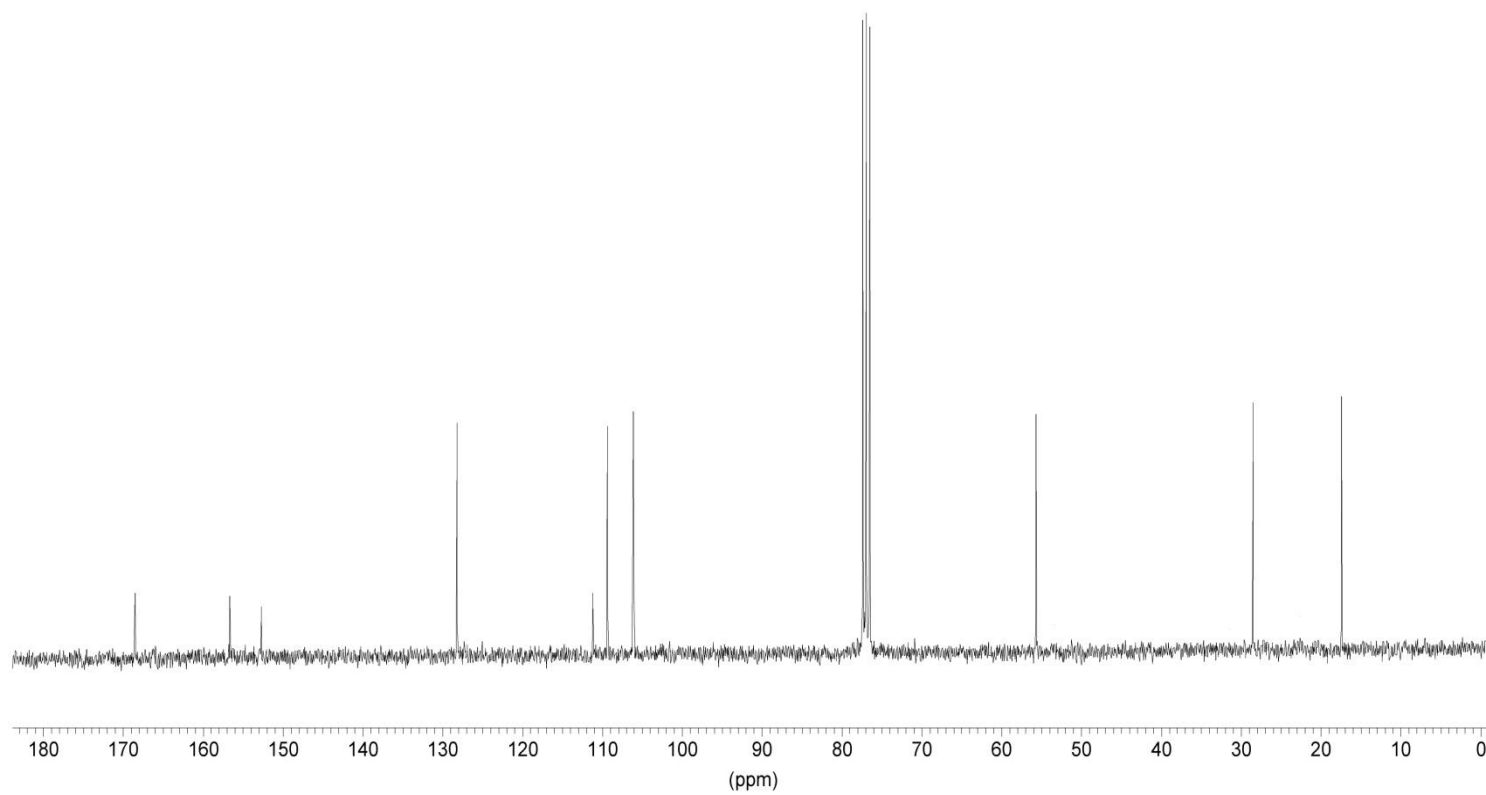


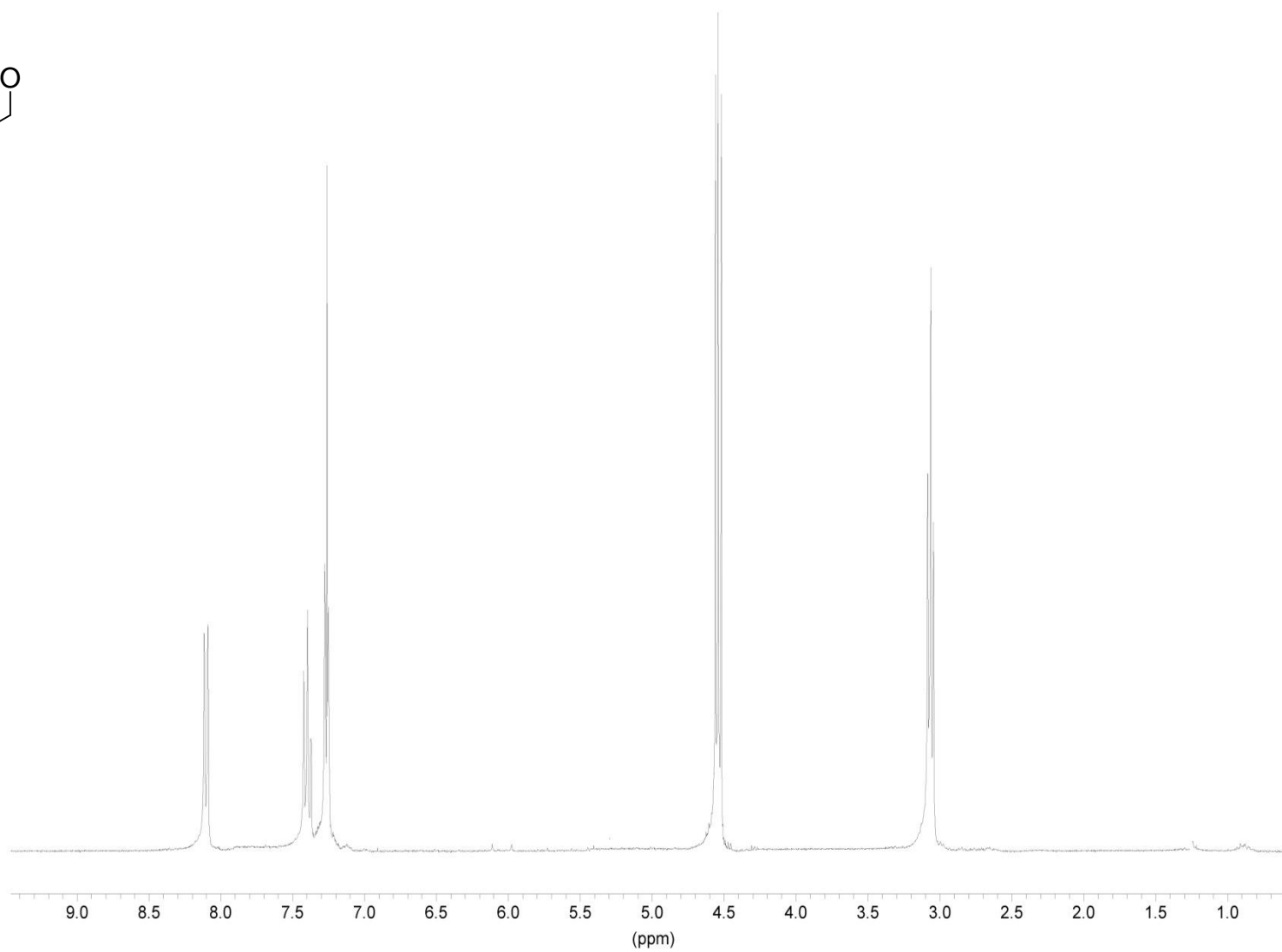
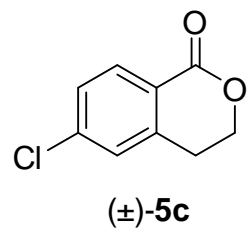
8b

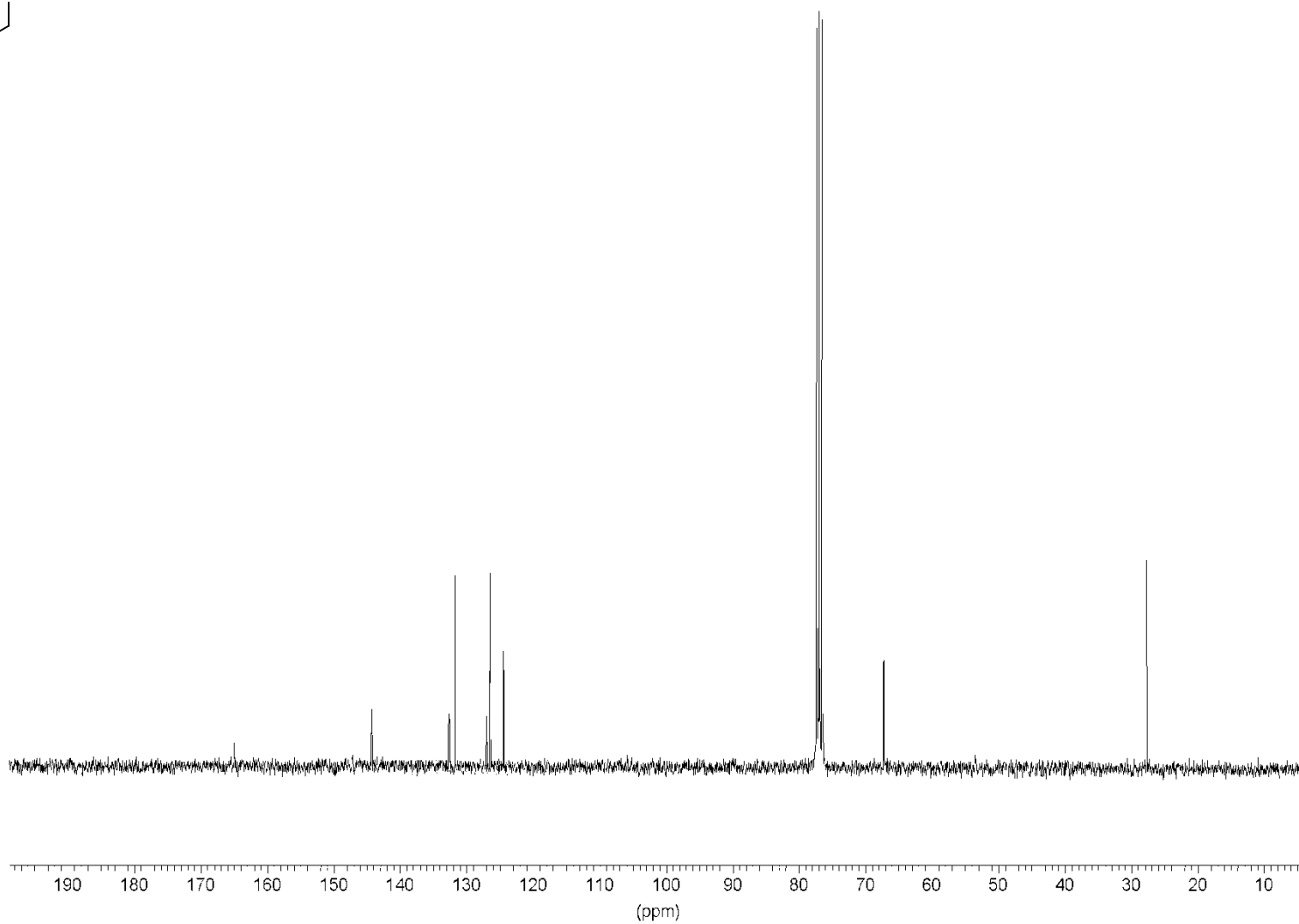
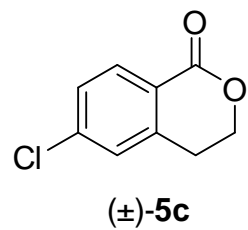


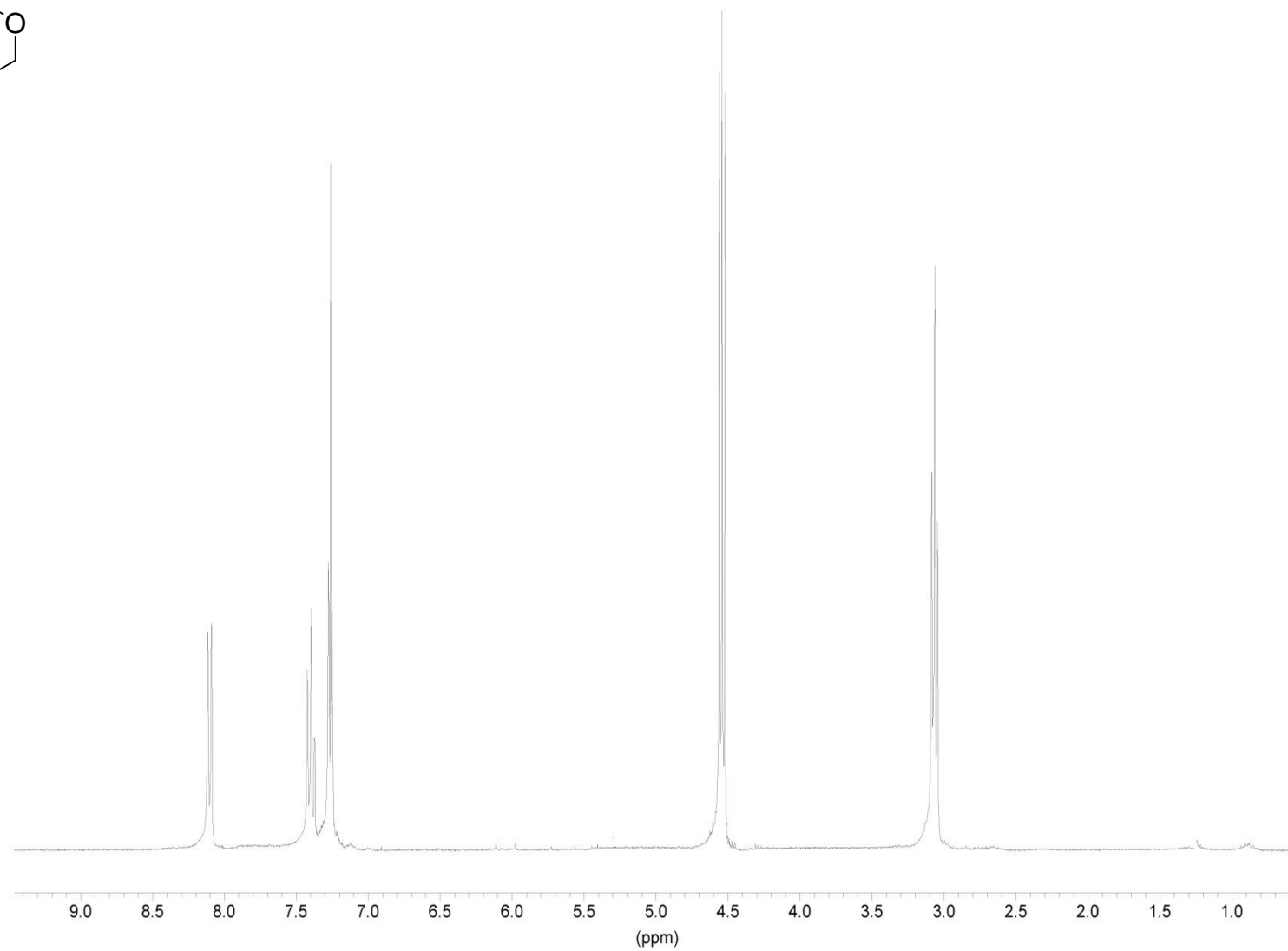
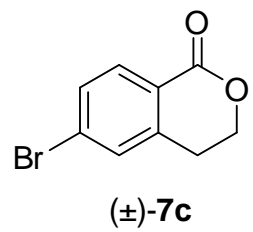


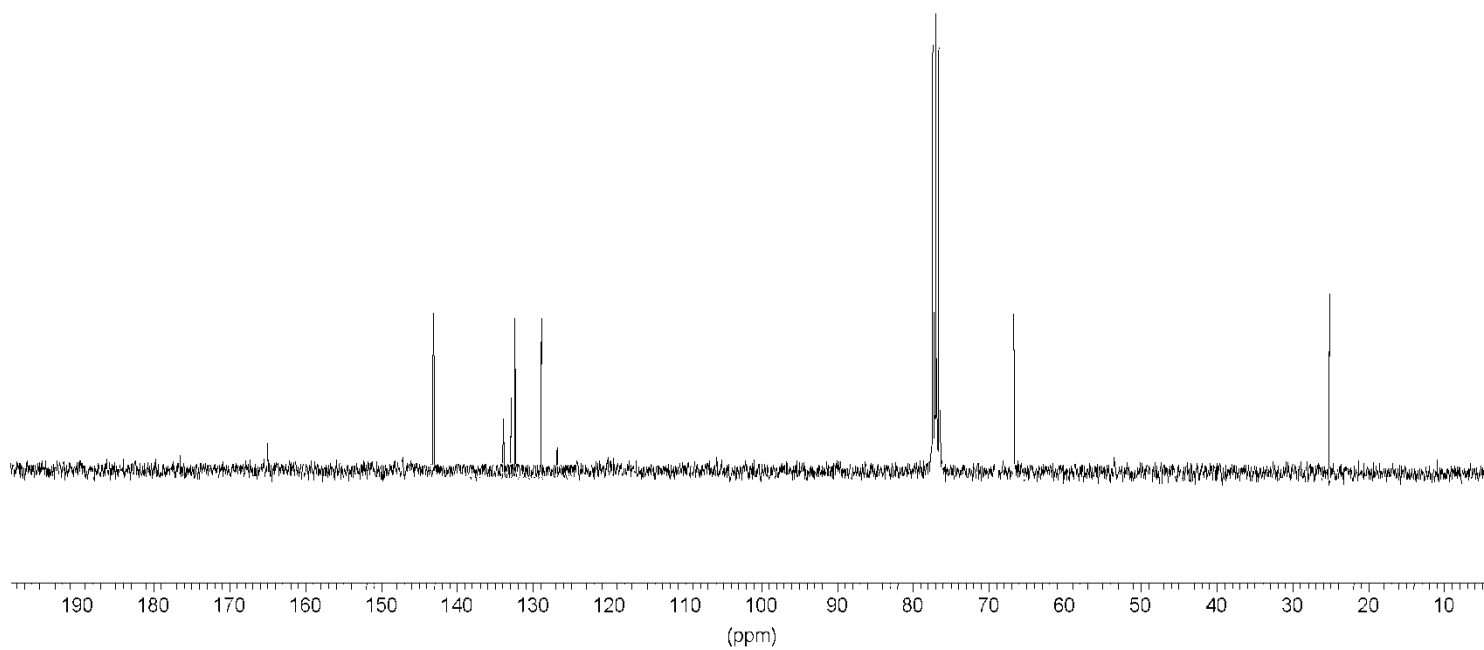
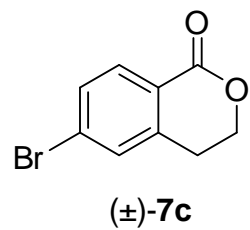
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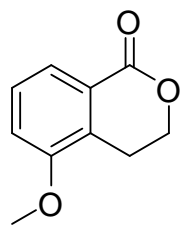




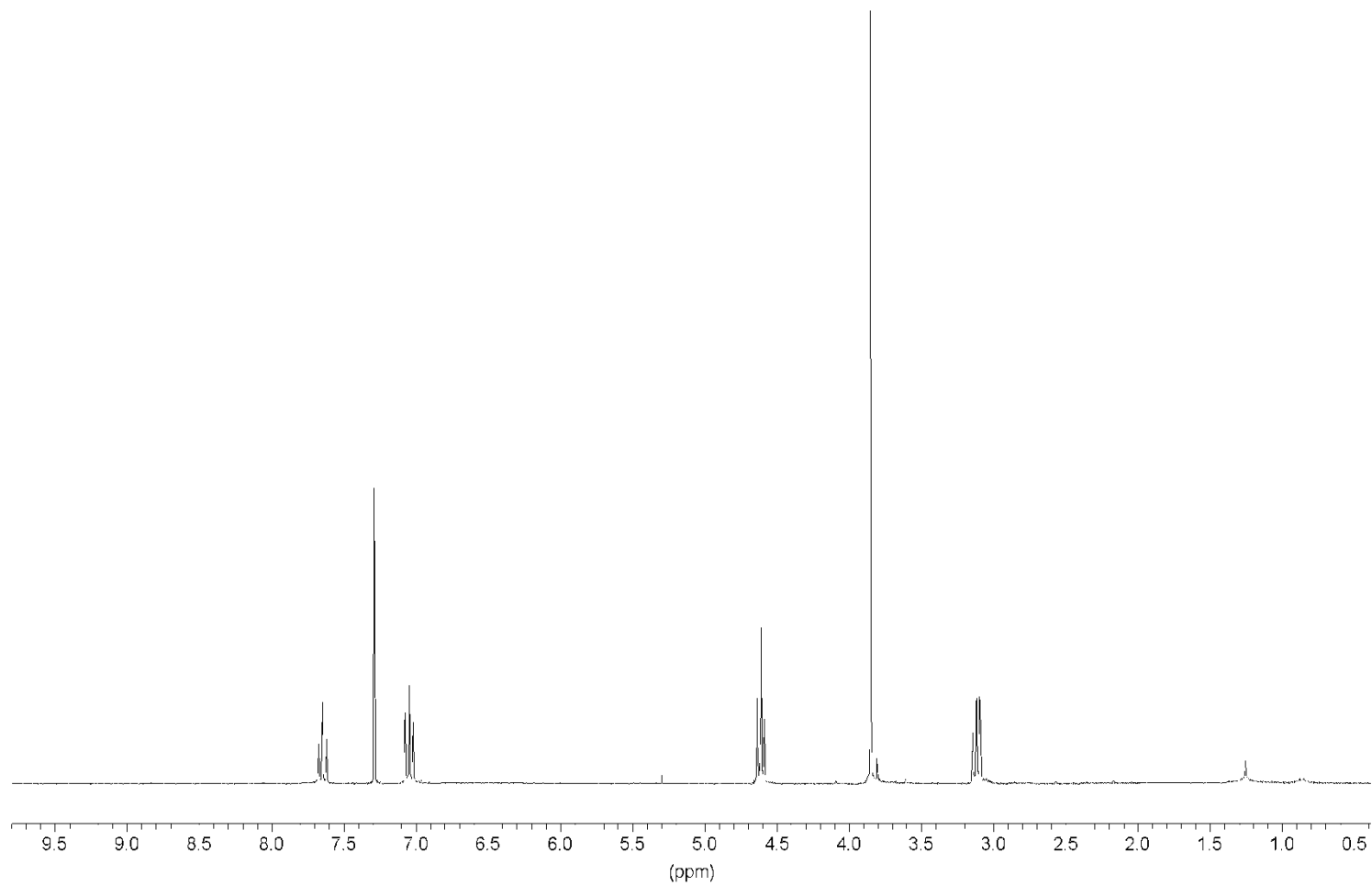


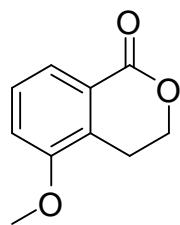






(±)-8c





(±)-8c

